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VAPOR PRESSURE OF SOLID HD

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14. ABSTRACT
The vapor pressure of the vesicant agent bis-(2-chloroethyl) sulfide (HD), has been measured between –25 and +20 °C using vapor saturation methodology. This work reports the vapor pressure of solid HD for the first time.

15. SUBJECT TERMS

bis-(2-chloroethyl) sulfide (HD)	HD volatility	Solid-state vapor pressure
HD vapor pressure	Heat of fusion	Heat of sublimation

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PREFACE

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CONTENTS

FIGURES

TABLE

1.   INTRODUCTION

        Numerous investigators have reported the vapor pressure of liquid bis(2-chloroethyl) sulfide[1-8] (HD) using a variety of methods, including between 14.9 and 75.8 °C using dynamic gas saturation,[3] between 17.8 and 31.9 °C using a manometer,[3] between 25.0 and 45.0 °C using air transference,[2] between 54.8 and 81.7 °C using a U-tube,[3] and between 80.0 and 216.6 °C using boiling point measurement.[2] The literature data reported for liquid HD are internally consistent and have been described by an Antoine equation fit by Penski.[9,10] To the best of our knowledge, the vapor pressure of solid HD has not been reported. It is not suitable to extrapolate liquid phase HD vapor pressure data below its melting point, 14.5 °C, owing to the anticipated change in slope due to the heat of fusion. Buckles[8] has estimated the HD vapor pressure below the melting point using the measured heat of fusion, however. In this work, we report the low-temperature HD vapor pressure using a modified vapor saturation method developed recently and exploited to measure the vapor pressure of numerous CW agents and simulants in the ambient temperature range.[11-13] Our modifications of the vapor saturation method included use of a vapor concentrator and flame ionization detection gas chromatography to allow precise measurement of volatile components of direct interest. These measurements, which are made in the presence of both higher and lower volatility impurities, eliminate confusion associated with approaches such as mass loss, which cannot discriminate among the target species and impurities. Flame photometric detection has also been used to increase projected sensitivity to below the part-per-trillion range. The vapor saturation method has been further modified recently to facilitate measurement of volatility as a function of both temperature and humidity.[14-15] The latter body of work has demonstrated proof of principle using the nerve agent simulant, dimethyl methylphosphonate (DMMP), and will be extended to the measurement of the volatility of CW agents. Initial attempts to investigate GF volatility as a function of ambient humidity have been unsuccessful owing to a hydrolysis reaction. In our efforts to measure the vapor pressure of HD in similar fashion, it came to our attention that the requisite fundamental data (i.e., low-temperature vapor pressure data of HD), were not available in the literature.

2.   EXPERIMENTAL PROCEDURES

        Saturated HD vapor streams were generated by flowing dry nitrogen carrier gas at 25.0 standard cubic centimeters per minute (sccm) through a glass vessel (i.e., saturator, containing solid HD), shown schematically in Figure 1. The saturator has been described in detail in a previous report from this laboratory.[12]
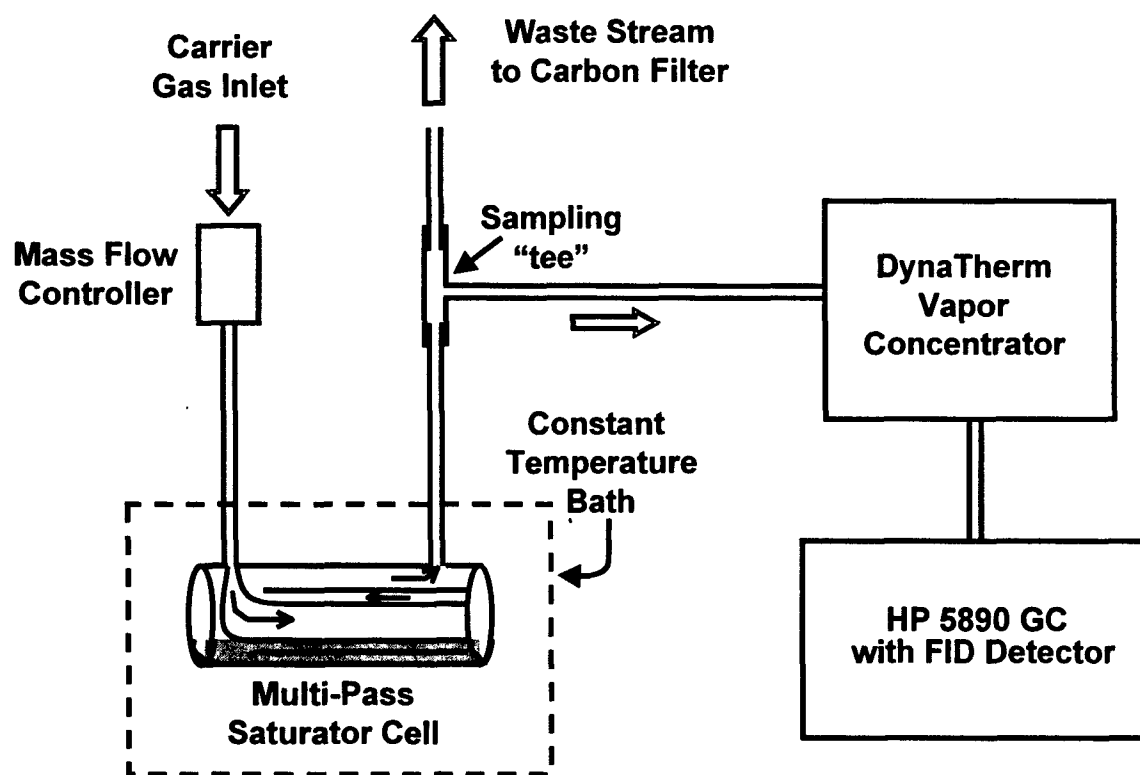
Figure 1. Schematic of Data Acquisition System Used to Measure Solid HD Vapor Pressure

In this work, the saturator was loaded with 5 g of neat liquid HD, Chemical Agent Standard Analytical Reference Material (CASARM), Lot Number HD-U-9040-CTF-N. The HD sample was purged with dry nitrogen for three days to remove volatile impurities and then the liquid phase was analyzed by Gas Chromatography (GC) using a Thermal Conductivity Detector (TCD). Integration of the area under the HD peak resulted in an area amounting to 98.5% of the total area, and we have taken that value to be the liquid phase purity in subsequent data analyses. The HD sample used in this work was also analyzed immediately after the data were collected by the same method with no observable change in purity.

The saturated HD stream, generated by flowing dry nitrogen carrier gas through the saturator at 25 sccm, was sampled by drawing 5-10 sccm of the saturator effluent to the Dynatherm concentrator, a modified ACEM Model 900 (Dynatherm Analytical Instruments Incorporated, Kelton, PA) system containing a tenax adsorbent tube. The flow rate was controlled using a calibrated 10-sccm mass flow controller (Tylan Model FC-280, Austin, TX), which was connected to a vacuum pump and allowed to sample for two to 50 min, depending on the amount of HD to be collected (i.e., the flow rate and temperature). The saturator effluent was sampled at a "tee" connection three cm downstream of the saturator constant-temperature bath. The sampling line was constructed of 1/16-in. o.d., 0.040-in. i.d. Sulfinert® tubing (Restek Corporation, Bellefonte, PA). All connectors between the saturator effluent line "tee" and the

concentrator were fabricated from 316 stainless steel. The concentrator sampling line between the "tee" and the ACEM was heated to ca. 80 °C to reduce sample line adsorption losses and thus reduce the time needed to achieve steady state conditions following sample temperature changes. The ACEM 900 valve box, external six-port valve, and transfer line to the GC were maintained at 100 °C. The sample was concentrated by the ACEM 900 using the following operating parameters. The temperature of the 10-mm o.d. tenax collection tube was maintained at 40 °C during the variable 2- to 50-min sample collection time. A 1-min purge using dry nitrogen was employed as the next step of the sampling process. The sample was rapidly heated to 275 °C under a flow rate of 20 sccm dry nitrogen for 5 min and transferred to the ACEM 900 tenax focusing trap, which was maintained at 40 °C. Transfer continued for an additional minute as the 10-mm o.d. tenax collection tube cooled. The tenax focusing trap was then rapidly heated to 300 °C under a flow of 8 sccm dry nitrogen for 5 min to effect sample transfer to the GC column. The saturator was operated at as high as 50 sccm with no change observable in the FID response to demonstrate that the concentration of HD is independent of flow rate and that the system had attained vapor-liquid or vapor-solid equilibrium. Ambient atmospheric pressure and saturator temperature were measured as described in an earlier report.[12]

The GC column (Restek Corporation, Bellefonte, PA), a 30-m x 0.53-mm i.d. fused silica column with 1.0-μm RTx-1701 (14% cyanopropylphenyl - 86% dimethyl polysiloxane) film, was programmed to go from 40 to 225 °C at a rate of 10 °C/min after a 1.5-min post-injection interval. A Hewlett Packard (HP) Model 5890 Series II GC equipped with a flame ionization detector (FID) was used as the analytical detection system in this work. Nitrogen was used as the GC carrier (8 sccm) and detector make-up (22 sccm) gas. Combustion gases were air (400 sccm) and hydrogen (30 sccm). Using the instrumentation and operating conditions described, HD eluted at 12.5 min, which corresponds to a GC elution temperature of 150 °C.

Two stock solutions were prepared for calibration of the ACEM 900–5890 FID system by adding an accurately measured amount of analyte to the appropriate solvent and correlating the resulting GC integrated peak areas to analyte mass. Twenty-five microliters (μL) of neat CASARM HD (98.5% pure, sampled from the saturator) were added to about 8 mL of hexane (Capillary GC Grade, Aldrich Chemical Company, Milwaukee, WI) using a 25-μL Drummond Model 525 Digital Microdispenser (Drummond Scientific Company, Broomall, PA), then diluting to 10.0 mL with hexane. Converting this volume of HD to mass using the liquid density at room temperature (1.2712 g/mL at 22.5 °C) and correcting for HD purity (98.5%) resulted in a solution with a concentration of 3.13 μg HD/μL hexane. The second calibration standard was prepared in a similar manner. Ten microliters of the 98.5% pure CASARM HD were added to about 8 mL of hexane using a 10-μL Hamilton Model 701 MICROLITER™ syringe (Hamilton Company, Reno, NV), then diluting to 10.0 mL with hexane. Converting this volume of HD to mass using the liquid density at room temperature and correcting for HD purity resulted in a solution with a concentration of 1.25 μg HD/μL hexane.

All calibrations were performed during the same day that the standards were prepared. The ACEM 900–5890 FID system was calibrated by making 1- to 5-μL injections of HD-hexane standards into the distal end of the heated (80 °C) 1/16-in. o.d., 0.040-in. i.d. Sulfinert® tubing, which was supplied with dry nitrogen carrier gas at a flow rate of 10 sccm.

The ACEM 900 and GC operating parameters were identical to those used for experimental data acquisition with one exception. The ACEM 900 external sampling time for calibration data was always maintained at 15 min to allow sufficient time for HD transfer to the tenax sampling tube. The resulting calibration curve is shown in Figure 2 and was generated by plotting FID area counts versus mass of HD injected for the combined high standard and low standard calibration runs. Equation 1 describes the combined calibration data set most accurately given the constraint that the calibration curve go through the origin and be limited to a quadratic for ease of analysis.

$$A = -0.007198 \cdot m_{HD}^2 + 1.668432 \cdot m_{HD} \tag{1}$$

where

m_{HD} = mass of HD (μg) injected
A = GC area (in millions of area counts)

Vapor pressure values are inferred from the measured data using Equation 2, as described elsewhere.[12]

$$VP_{HD} = P_{ambient} \cdot n_{HD}/(n_{HD} + n_{carrier}) \tag{2}$$

where

· VP_{HD} = vapor pressure of HD calculated from measured data

$P_{ambient}$ = ambient atmospheric pressure

n_{HD} = number of moles of HD, measured by GC-FID

$n_{carrier}$ = number of moles of nitrogen carrier, measured as described above

3.   RESULTS AND DISCUSSION

The Table lists the HD vapor pressures measured in the present work at temperatures between -25 and +13 °C. Data reported in this work along with Penski's Antoine equation for liquid HD are depicted in Figure 3, which also shows the melting point of HD. Two data points were measured in the current work above the melting point to demonstrate agreement between our measurements and accepted literature values. The value observed at 20 °C was 9.12 Pa, which is within 0.4% of the value calculated using the Penski Antoine equation, 9.16 Pa, and the value observed at 15 °C was 6.04 Pa, which is within 3.74% of the value calculated using the Penski Antoine equation, 5.82 Pa. This agreement is considered to be excellent. In addition, the small residual difference in the latter (+0.22 Pa) is extremely close to the difference in calculated vapor pressures at the melting point using the liquid and solid phase correlations ($VP_{solid} - VP_{liquid} = +0.21$ Pa), suggesting that the agreement is actually better than indicated here.
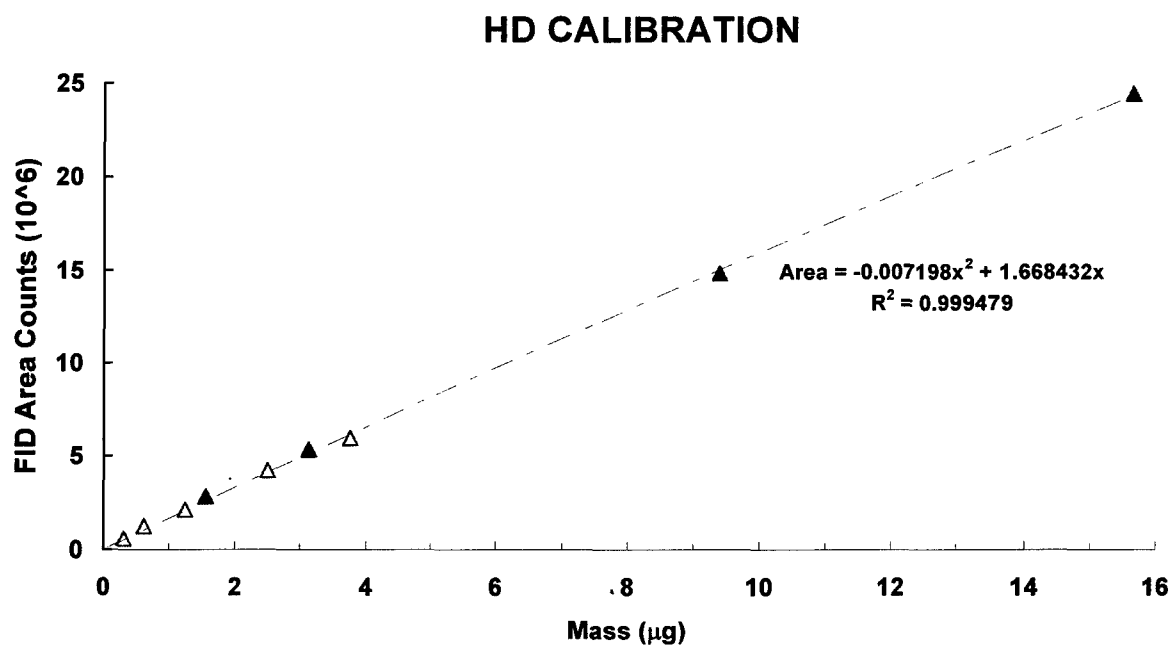
HD CALIBRATION

Figure 2. HD Calibration Curve and Analytical Equation. Filled triangles show data measured using 3.13 µg/µL standard, and open triangles show data measured using 1.25 µg/µL standard.

Table. Clausius-Clapeyron Coefficients, Solid HD Vapor Pressure Data Measured in this Work Using the Saturator Method, Calculated Vapor Pressure Using the Clausius-Clapeyron Coefficients, and Percent Difference Between Measured and Calculated Values. Heats of Fusion and Sublimation.

Clausius-Clapeyron Equation for Solid HD		
$\ln P \text{ (Pa)} = a - b/T(K)$		
a	35.585	
b	9731.98 K	
ΔH_{fusion}	4.0 kcal/mole	
$\Delta H_{sublimation}$	19.3 kcal/mole	

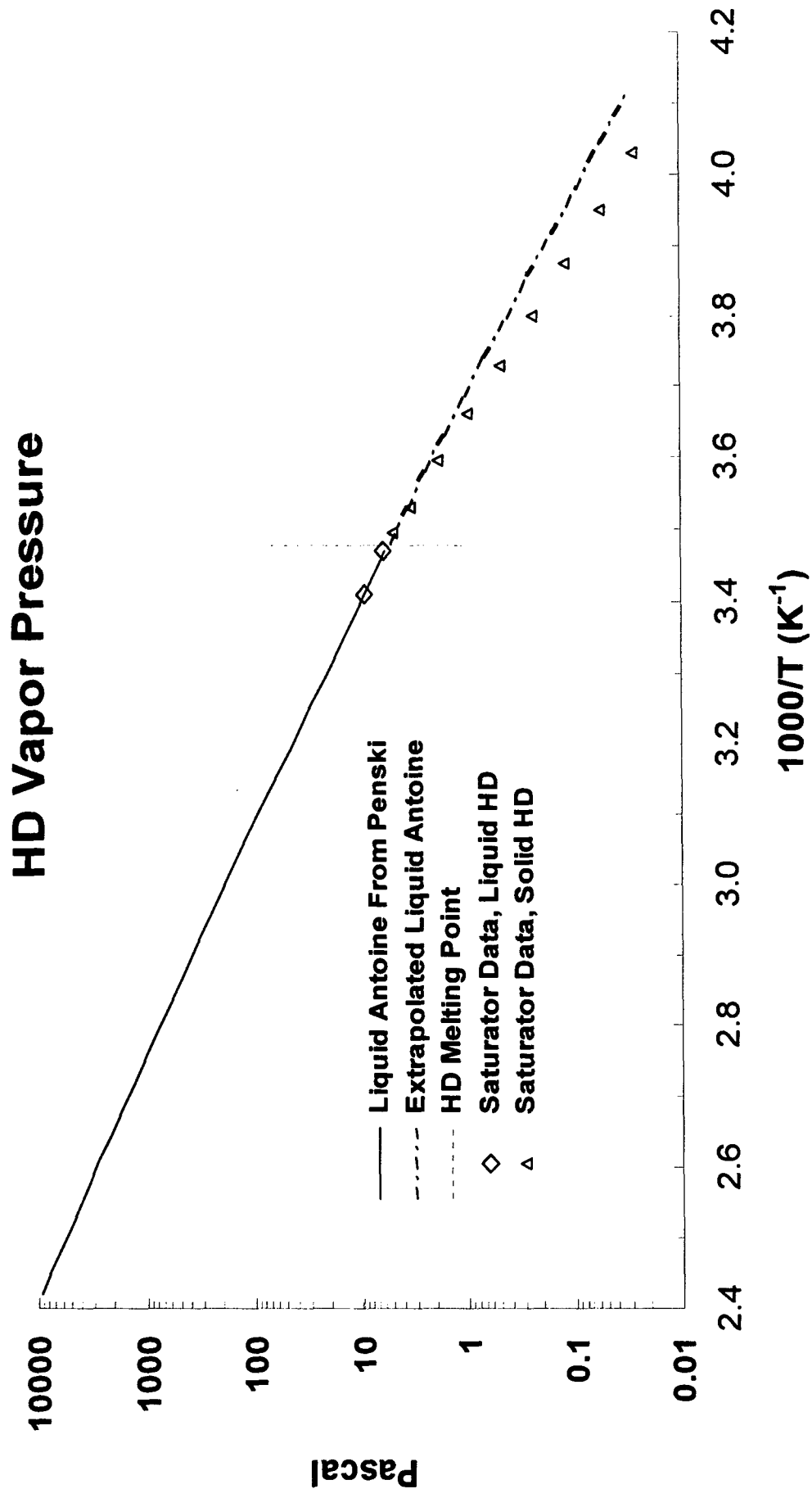| Temperature (°C)	Vapor Pressure (Pa)		Difference (%)
	Measured	Calculated	
13.0	4.81	4.83	-0.47
10.0	3.34	3.37	-0.76 ,
5.0	1.86	1.82	2.3
0.0	0.984	0.957	2.7
-5.0	0.490	0.493	-0.43
-10.0	0.241	0.247	-2.4
-15.0	0.118	0.121	-2.6
-20.0	0.0560	0.0573	-2.4
-25.0	0.0277	0.0264	4.6

11

Figure 3. Literature Antoine Correlation for Liquid HD and Liquid (diamond) and Solid (triangle) Saturator Vapor Pressure Data for HD. HD melting point is indicated by the dashed vertical line.

At the lowest temperature investigated in this work, -25 °C, the measured vapor pressure was found to be less than one-half of the value predicted by the Antoine equation based on liquid phase data. The discrepancy between data measured below the melting point and the predictions based on the liquid-phase data is caused by the heat of fusion contribution to the heat of vaporization (sublimation) and is discussed further below.

An Antoine fit to the solid-phase data was attempted; however, it was found that the agreement between measured and calculated data do not warrant a three-parameter fit, because the two-parameter fit listed in the Table and shown in Figure 4 describes the data equally well. This observation is attributed to the residual inaccuracy of the data and the narrow temperature range of the solid-state data. It should be noted that the average difference between calculated and observed data points for solid HD is 2.1%, which we believe to demonstrate very good experimental precision for the data. Figure 4 also depicts the correlation proposed by Buckles[8] for solid HD vapor pressure based on the projected heat of fusion and can be seen to be higher by 20.1% at -25 °C than observed in the present work.

The observation of a change in the slope of the vapor pressure curve at the melting point of a substance is to be expected. The slope of the vapor pressure plot is directly related to the heat of vaporization, and the change in slope is indicative of a non-zero heat of fusion, that is, the heat of vaporization of the solid has two contributions, which are the heat of vaporization of the liquid and the heat of fusion. The sum of those two components is also known as the heat of sublimation.

The heat of fusion can be inferred from the change of slope at the melting point using the Antoine **B** and **C** coefficients at the melting point for the liquid phase[10] and the Clausius-Clapeyron **b** coefficient for the solid phase determined in this work. The indicated solid phase heat of sublimation is 19.3 kcal/mole (independent of temperature), and the heat of vaporization of the liquid at the melting point is 15.3 kcal/mole, indicating a heat of fusion of 4.0 kcal/mole. This value compares very favorably to the value of 4.2 kcal/mole reported by Buckles.[8]

4.   CONCLUSIONS

Vapor pressure data and two-parameter correlation are reported for the first time for solid HD. The heat of fusion has been estimated to be 4.0 kcal/mole based on the change in slope of the liquid and solid phase vapor pressure plots at the melting point. The consistency between the currently observed data and that expected based on the earlier work provides significant confidence in the accuracy of the present data.
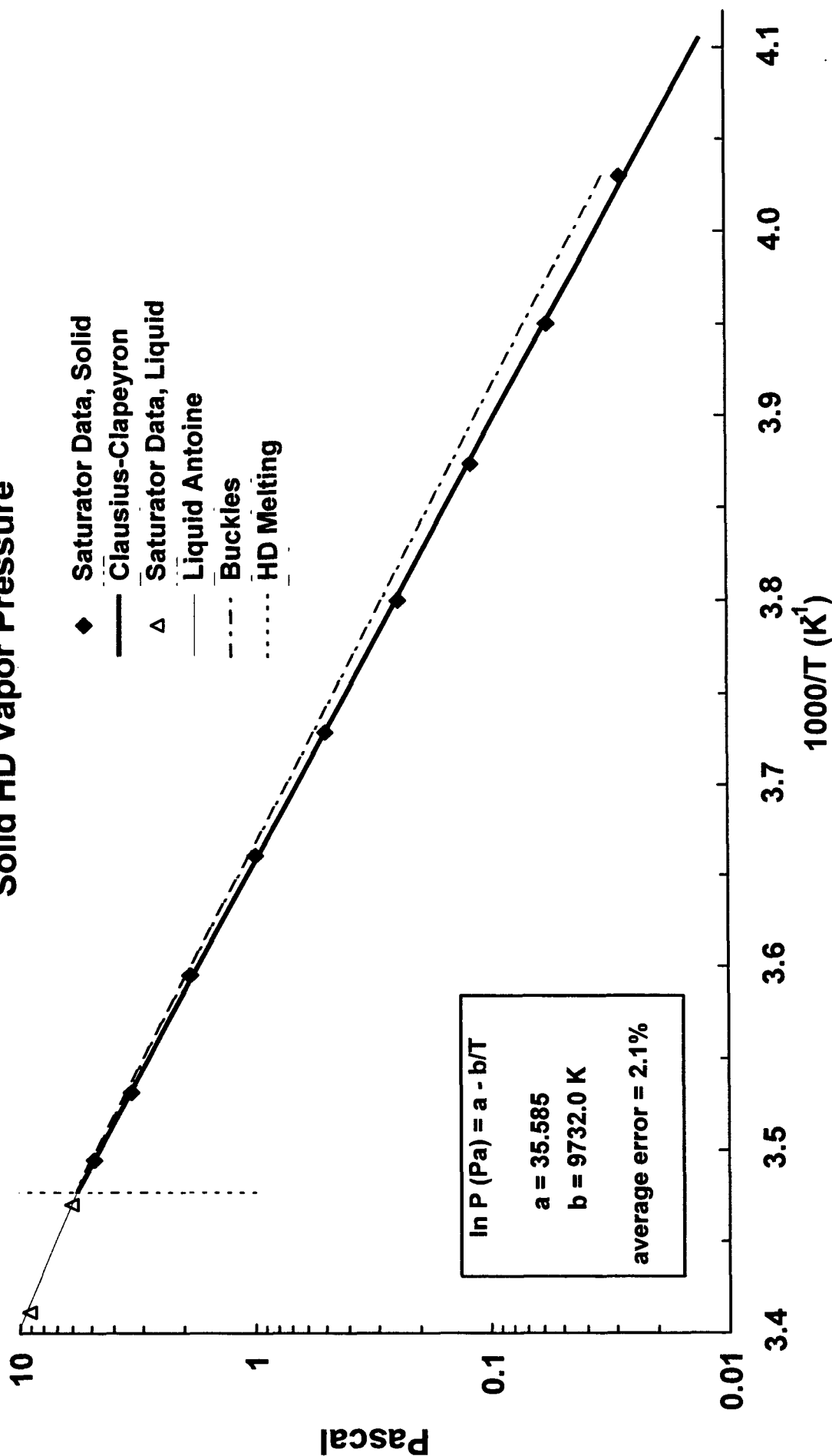
Figure 4. Vapor Pressure Data Measured for Solid and Liquid HD Using Vapor Saturation, Clausius-Clapeyron Constants and Fit, Buckles' Correlation, and HD Melting Point.

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